

Global Atmospheric O₂/N₂ Measurements from Isotope Ratio Mass Spectrometer Analysis

MICHAEL L. BENDER, JOHN T. ELLIS, AND MARK O. BATTLE

Graduate School of Oceanography, University of Rhode Island, Narragansett, Rhode Island 02882

INTRODUCTION

Measurement of atmospheric oxygen can provide important constraints on the global carbon cycle. When O₂ is monitored with sufficient accuracy, the monitoring is complemented with measurements of CO₂, and the observations are augmented with an atmospheric circulation model, it is possible to gain understanding about new production of organic matter in ocean surface water, the distribution of terrestrial sources and sinks of carbon, and the oceanic storage of anthropogenic CO₂ [Keeling *et al.*, 1993; Keeling and Shertz, 1992].

To this end, air sample collection began at BRW in December of 1992. Working in conjunction with SIO, we have also started collecting samples in SMO and from the top of the light tower at Cape Kumukahi, Hawaii (via the MLO station). Sampling at these two stations began in June of 1993. The samples collected at these CMDL stations supplement our ongoing acquisitions at Cape Grim, Tasmania; Baring Head, New Zealand; Sable Island, Canada; and Syowa, the Japanese coastal Antarctic station. The CMDL Carbon Cycle Division in Boulder, Colorado, performs the complementary measurements of carbon dioxide for all of these samples.

SAMPLING AND ANALYTIC TECHNIQUE

Samples are collected in 2-L glass flasks equipped with a pair of shaft-seal valves fitted with Viton o-rings. A small pump draws ambient air through a cold trap, drying the sample. The flask is flushed with at least 40 liters of dry air before being filled to a pressure of one atmosphere. Duplicate pairs of these flasks are collected biweekly at each site.

The O₂/N₂ ratio of air is measured using a conventional isotope ratio mass spectrometer. As with all such devices, the O₂/N₂ ratio is measured relative to some arbitrary reference. In our case, we use air collected by the CMDL Carbon Cycle Division at Niwot Ridge, Colorado, and stored in high-pressure aluminum cylinders. For use on the mass spectrometer, these cylinders are used to fill 70-L glass flasks that we refer to as working standards.

For analysis, gas from samples and standards is admitted into evacuated glass inlet lines. Each inlet is connected to the mass spectrometer by a 1-m length of fused silica tubing with an inside diameter of 25 microns. The volume of each inlet is adjustable with a manually controlled piston, allowing us to equalize the flow rates from the inlets by compensating for variation in collection pressure of the samples or depletion of the standard. The analysis of a flask consists of at least four expansions of each sample-standard comparison. Two of the expansions are carried out with one inlet-sample/inlet-standard pairing. The relationship is then reversed for the two remaining expansions. The spectrometer is configured to simultaneously measure masses 29 (¹⁵N¹⁴N) and 32 (¹⁶O₂). This coincident measurement of the two species, along with repeated switching between the sample and working standard, and long integration times, provides a high level of analytic precision.

We have chosen to express the relative changes in the O₂/N₂ in units of "per meg." This is similar to a percent change and is mathematically defined as

$$\delta(\text{O}_2 / \text{N}_2) = \left(\frac{(\text{O}_2 / \text{N}_2)_{\text{sample}}}{(\text{O}_2 / \text{N}_2)_{\text{standard}}} - 1 \right) \times 10^6 .$$

In these units, 4.8 per meg (1/0.2095) is equivalent to 1 ppm V since O₂ is 20.95% of air by volume. The procedure outlined above gives an analytic precision of approximately 4 per meg.

RESULTS

To date, we have collected roughly 1 year of data at BRW. The values of the O₂/N₂ measurements are presented in Figure 1, where the seasonal cycle is clearly visible with an amplitude of ~170 per meg. Preliminary results from Cape Kumukahi and SMO show seasonal cycles of smaller amplitude, but with less than a full year of data available, the size is hard to quantify. Our more extended records from Tasmania and New Zealand show a seasonal amplitude of ~90 per meg. Since the seasonal cycle comes from the combined effects of the ocean biosphere, thermal effects at

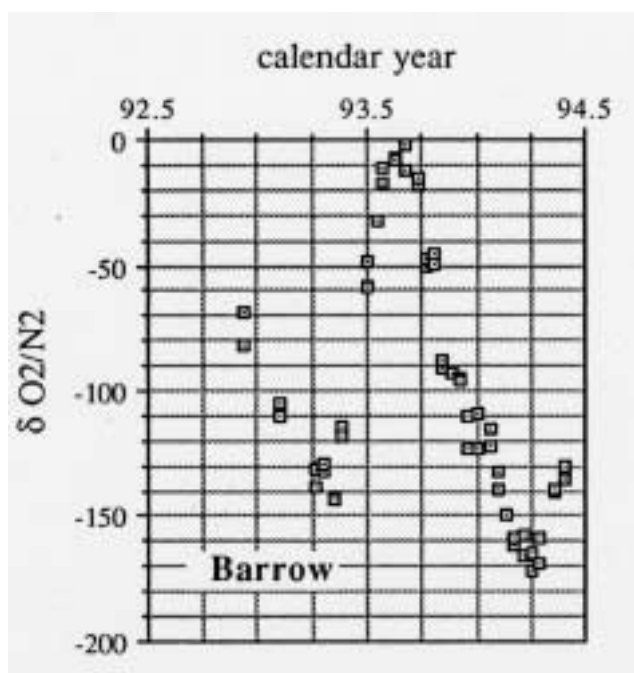


Fig. 1. The O_2/N_2 ratio as measured at the BRW station from late 1992 until mid 1994. The ratio is given as a difference (in units of per meg) from some arbitrary standard. At each point in time, two flasks are filled. The analysis of each flask's contents is shown on the plot, giving some indication of the overall reproducibility of the procedure. The seasonal cycle has an amplitude of ~ 170 per meg. The interannual decrease of O_2 also seems to be visible, but is not yet quantifiable.

the air-sea boundary, and the terrestrial biosphere, different cycles in the northern and southern hemispheres are to be expected.

With longer records at all of the collection sites, we will be better able to constrain short-term interannual variation and the long-term consumption of O_2 due to human activities, as well as the distribution of carbon sources and sinks, terrestrial and oceanic. We look forward to the extension of this record in the coming years.

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